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INDIANA UNIV BLOOMINGTON DEPT OF CHEMISTRY

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SIMPLIFIED APPARATUS FOR ROUTINE SELECTIVE SPECTRAL-LINE MODULA--ETC(U)

SEP 77 R L COCHRAN, G M HIEFTJE

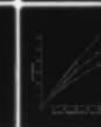
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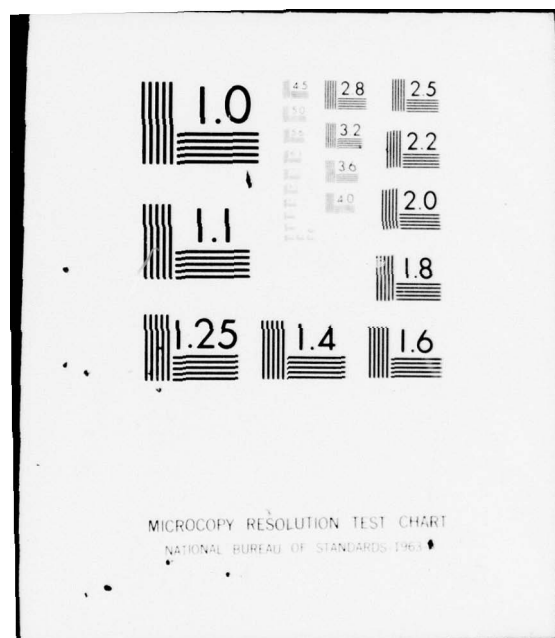
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20. Abstract (continued)

tainable using a line source within the same system. Detection limits found for a series of elements with the present SLM design are shown to be little improved over those for conventional, medium-resolution, continuum-source atomic absorption spectrometry. Important noise characteristics of the present SLM device are examined.

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TECHNICAL REPORT NO. EIGHT

Simplified Apparatus for Routine Selective
Spectral-Line Modulation Atomic Absorption Spectrometry

by

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The idea of using a spectral continuum source in atomic absorption spectrometry (AA) has long appealed to analytical chemists. Such a combination offers the promise of single-source qualitative and multi-element analysis, while retaining the simplicity of conventional AA. Accordingly, a number of both theoretical (1-4) and experimental (5-10) treatments have appeared describing continuum-source atomic absorption (AAC) instruments which employ a medium-resolution monochromator. Although such systems maintain the cost-effectiveness of continuum-source AA relative to line-source AA (AAL), the studies have emphasized the problems associated with medium-resolution AAC. These problems include poor detection limits, severe working curve non-linearity, and a high susceptibility to line and broad-band absorption and stray-light interferences.

To remedy these problems, several workers have employed spectral sorting devices which offer such high resolving power that resolution of individual atomic absorption line profiles becomes possible (11-16). Of these instruments, the most promising from the standpoint of practical analytical AAC appears to be one employing an echelle monochromator, wavelength modulation via a quartz refractor plate, and a 150-W Eimac lamp. While this echelle system does much to improve the analytical utility of AAC, it still suffers to some extent from stray-light interference, and requires an expensive monochromator to achieve the necessary resolution.

A second approach to performing analytically useful AAC has been through selective modulation techniques (16-20). With this approach, the high effective resolving power needed for AAC can be obtained through selective amplitude modulation of an atomic absorption line of interest followed by frequency-selective monitoring of only the spectral region containing that atomic absorption line. In selective-modulation AAC, a medium-resolution monochromator

can be employed because it serves only to minimize stray and background radiation (similar to the monochromator's role in AAL), and the expense of a high-resolution spectral sorting device is avoided.

A new approach to performing AAC using a selective spectral-line modulation (SLM) technique was recently described (20). In that approach, discrete droplets of a metal salt standard solution are periodically introduced into a modulating flame via a droplet generator (21). The atom clouds so produced move within the flame through a beam of continuum radiation, thereby selectively modulating those atomic absorption lines which are characteristic of the atoms within the clouds. The continuum source and modulating flame combination serve to replace the modulated line source in an otherwise conventional AAL spectrometer.

This SLM system was shown to provide improved working curve (absorbance vs. sample solution concentration) linearity compared to conventional AAC, and absorption sensitivities approaching those typical of AAL. In addition, the system was shown to be amenable to multi-element AA analysis, to exhibit relative freedom from narrow-line spectral interferences, and to provide a simple means of background correction.

In the present paper is presented an alternative instrumental system for use in the SLM method, which is better suited to routine analytical applications. The new SLM instrument replaces the droplet generator and Meker-type modulating flame with a more conventional double-beam optical design. In this design, a conventional nebulizer/spray-chamber and slot burner combination forms the modulating atom cell, and a mirrored chopper is employed to direct the continuum radiation alternately around or through this atom cell (see Figure 1). In this way, a selective modulation function is performed in a manner similar to that provided by the modulating vapor clouds in the previous system (20). In

addition, a 300-W Eimac xenon arc lamp is used as the primary source, providing many times the usable radiation of the conventional 150-W xenon arc lamp previously used.

The routine operation of the new SLM system is described, and several optical design considerations resulting from incorporation of the Eimac lamp in the device are discussed. Detection limits obtained with the new arrangement are evaluated and compared to those found for conventional AAC, and important noise characteristics of the SLM technique are considered.

EXPERIMENTAL

Optical System. The optical design employed in the new SLM system is depicted in Figure 1, with details concerning the individual components and experimental conditions summarized in Table I. The signal processing scheme used here has been described elsewhere (20), and differs only in the means by which the synchronous reference signal is derived. As shown in Figure 1, the reference detector in this system simply monitors the beam A radiation which is periodically transmitted by the mirrored chopper.

The optical design of the SLM system was dictated largely by the strict optical path requirements of the two slot burners employed, and the special optical considerations which proved necessary to utilize the Eimac lamp to greatest advantage. Studies in this laboratory (22) have shown that, while the 300-W Eimac arc lamp provides an output beam power which is up to 37 times that available from a conventional 150-W xenon short-arc lamp, several less desirable characteristics of the lamp require close attention

in this particular application. Because the relative noise component of the lamp's output radiation varies as much as a factor of five depending upon the spatial portion of the output beam which is sampled, the first lens in the system (L_1) is stopped down to 1 cm diameter by aperture A_1 (see Figure 1) to provide the desired spatial selection. In this way a 1 cm cylinder of collimated radiation is accepted from the bottom of the lamp, the region found to exhibit the least relative noise (best output radiant-power-to-noise ratio).

Furthermore, due apparently to the rather poor optical quality of the Eimac lamp's internal parabolic reflector, the image produced when the arc radiation is brought to a focus via a condensing lens is rather diffuse and poorly defined. This situation is contrary to that required for optimal sensitivity and linearity in analytical atomic absorption using a slot flame. To overcome this difficulty, the Eimac radiation is first focused onto a 1 mm field stop which effectively serves as a well-defined, near-point source for the remainder of the optical system. Although considered necessary, this procedure results in an estimated 60% radiant power loss due to the diffuse nature of the focussed Eimac beam.

Lens L_2 forms an image of the 1 mm field stop near the center of the sample flame, and lens L_3 renders the radiation approximately collimated again, before it encounters the beam splitter and is divided between beams A and B for the selective modulation process. The collimated radiation which enters beam A at the beam splitter and passes through the modulating flame is about 4 mm in diameter.

The mirrored chopper and modulating flame in Figure 1 perform selective modulation in a way similar to the periodically produced droplet clouds in the earlier system (20). The chopper alternately directs beam A and beam B through the final condensing lens, L_4 ; continuum radiation passing

through beam A will undergo selective atomic absorption by the atoms in the modulating flame, while radiation will pass through beam B unchanged. Therefore, by alternately observing the two beams, a selective modulation process takes place. In another view, the "combination source" discussed in the previous paper (20) consists here of the Eimac continuum source, modulating flame, and double-beam optical arrangement.

Lens L_4 focusses the chopped radiation onto the monochromator entrance slit, slightly underfilling the monochromator entrance aperture to reduce stray light within the monochromator. The nulling aperture, A_2 , enables nulling of background modulation, which will be discussed in the following section.

Operating Procedure. To begin normal operation, the Eimac arc is struck, both flames are lit, the chopper motor is turned on, and solvent aspiration into both flames is begun. During a 5-10 minute warm-up period, the monochromator wavelength is approximately tuned to the desired analytical line, and the photomultiplier tube voltage and preamp gain are set to previously determined values. Unlike the previous SLM system (20), no tuning of the modulating system for proper operation is required here, thus saving time and adding simplicity. Because the operating frequency and phase relationships in the present modulating system are constant, no adjustment of lock-in or frequency-selective amplifiers is required as part of the start-up procedure.

The photomultiplier shutter is next opened and the nulling aperture is adjusted to compensate for any broad-band modulation caused by absorption of the modulating flame itself at some wavelengths, or by poorly matched transmittance and reflectance of the beam splitter. Fine adjustment in the nulling procedure can also be performed via the zero-suppress control of the lock-in

amplifier. Although the need for this nulling procedure is a drawback of the present SLM system, particularly in applications requiring wavelength scanning, an improved beam splitter or use of two phase-related choppers in place of the beam splitter and chopper could significantly reduce the problem. After the nulling operation, the lock-in amplifier output represents the 0% transmittance of the system and the strip chart recorder is set accordingly, as in a conventional AAL instrument.

Finally, a modulating solution containing a preselected concentration of the element(s) to be determined is aspirated into the modulating flame, producing a lock-in amplifier output which is recorded and represents the 100% transmittance level (or effective incident power, P_0) of the combination source. The analyte, standard, and blank solutions can then be aspirated consecutively, and resulting transmittances (or effective transmitted combination source powers, P) recorded. From these transmittance values, absorbances can be calculated, working curves constructed, and analyte concentrations determined.

Analyte Emission Correction. In the present system, as in conventional AA instruments, it is necessary to correct for analyte atom emission in the sample flame. This correction is ordinarily accomplished through modulation of the primary source, and could be achieved by modulation of the Eimac source here. However, for the elements explored in this work using an air/C₂H₂ flame, the atomic emission from the sample flame proved negligible in all cases, and the atomic emission from the modulating flame proved significant only in the case of calcium.

Because the emission from the modulating atoms is 180° out of phase from their absorption, any detected emission is automatically subtracted by the

lock-in amplifier from both the SLM P_0 and P levels seen on the recorder, causing an error in the observed sample transmittance and calculated sample absorbance. To correct for modulating flame emission in the case of calcium, the lamp was blocked while the modulating solution was being aspirated, and the resulting lock-in amplifier output (generated only by the modulating atoms' emission) was added to the recorded P_0 and P values before absorbances were calculated. Because the Eimac radiation is used in providing the lock-in amplifier reference signal, an auxiliary reference signal had to be used to monitor the emission.

Such emission interference points out the need for either double modulation (23), involving modulation of the source in addition to use of the chopper, or a gated detection scheme similar to those used in commercial double beam AAL units, employing modulated hollow cathode lamps. The need for such an emission rejection scheme is expected to become greater when hotter N_2O/C_2H_2 flames are employed in this system.

Reagents. Stock solutions were prepared as suggested by Dean and Rains (24), using reagent-grade salts and acids as required. Analytical standards were prepared by suitable dilution of these stock solutions.

Detection Limit Calculation. In determining the SLM detection limits, the system was operated in the way just described with a lock-in amplifier time constant (τ) of 3 seconds. An aqueous sample solution of the element of interest containing a concentration equal to 10-50 times the detection limit was aspirated into the sample flame and values of P_0 and P were recorded on the strip chart recorder. Four sets of P_0 and P measurements were taken for each element, with the signals being monitored for at least 20τ for each trial. Detection limits were calculated using average values of $(P_0 - P)$ and N_{rms} (calculated as one-fifth N_{p-p}) obtained from these trials.

The modulating solution concentrations for most of the elements examined were chosen to provide about a 6% modulation of the integrated radiant power striking the photomultiplier (i.e., a 6% modulation depth). For lead (216.9 nm) and zinc, modulation depths were increased to about 9% in order to counteract the effects of increased shot noise and flame transmission flicker noise at the short absorption wavelengths of these elements.

AAC detection limits were recorded using the same equipment and optics as for SLM, except that a chopper was inserted between lens L_1 and the field stop (see Figure 1), to modulate the Eimac radiation at 480 Hz. A separate lamp and photodetector provided the needed lock-in reference signal for this work, and the lock-in amplifier zero-suppress control provided zero offset for the scale expansion needed to measure the AAC ($P_0 - P$) values accurately. In this configuration, the mirrored chopper was fixed in position to constantly transmit beam B, and neither beam A nor the modulating flame were used. Significantly, the presence of the beam splitter during the determination of AAC detection limits resulted in utilization of only approximately 35% of the continuum radiation. However, the SLM system actually observes a similar fraction of the available radiation at any given time.

Both AAC and SLM detection limits were calculated as suggested by St. John, McCarthy, and Winefordner (25) to be that concentration giving a ($P_r - P$) value 1.85 times the root-mean-square noise, based upon four trials and a 99% confidence level.

Stray Light Check. Because of the large radiant powers and broad spectral output of the Eimac lamp, stray light within the medium-resolution monochromator poses a possible problem in the new SLM apparatus. The magnitude of the stray radiation within the medium-resolution monochromator at various

wavelengths was checked using the ASTM recommended method (26). Because of the poor photomultiplier response and reduced source output below about 250 nm, stray light at these short wavelengths is expected to cause the greatest problem and was given the most attention.

RESULTS AND DISCUSSION

Replacement of the droplet generator (20) with a more conventional means of accomplishing selective modulation provides the new SLM system with increased dependability, simplicity of operation, and reduced cost. The system's analytical performance and its interference, noise, and fundamental operating characteristics are discussed in this section.

Sensitivity and Linearity. As discussed earlier (20), the sensitivity (working curve slope) exhibited by the SLM technique is greatly affected by the concentration of the element of interest used in the modulating solution. Figure 2 shows three Ca calibration curves which were obtained using the present SLM system with modulating solution concentrations of 5, 10 and 20 $\mu\text{g/ml}$ for curves A, B, and C, respectively. These curves clearly demonstrate that a reduction in both absorption sensitivity and linear range occurs as modulating solution concentration is increased. This result is not unexpected. Simple modeling of the SLM process, assuming Gaussian absorption line profiles for both the sample and modulating atoms, indicates that such a trend with increasing modulating atom concentration can be related to the increased fraction of the radiation absorbed at the peak of the atomic absorption line. A more complete description of this model will be published later. For modulating solution concentrations high enough that most of the radiation at the

peak of the atomic absorption line is absorbed, self-absorption broadening is also expected to play an important role (27, 28) in determining SLM sensitivity and linearity. Unfortunately, decreasing the modulating solution concentration to optimize sensitivity and linearity also reduces the size of the 100% transmittance (P_0) signal measured in the SLM process, and thus worsens the signal-to-noise ratio (S/N) of the sample transmittance measurement.

The Ca working curve sensitivity and linear range obtainable with the present SLM system is compared to those obtainable with the droplet-generator-based SLM system (20) and with a Ca hollow cathode lamp (AAL) in Figure 3. In the figure, the Ca AAL working curve was obtained using a modulated Ca hollow cathode source with the optical system and sample flame and nebulizer of the present SLM system. Both SLM curves were obtained using modulating solutions which were chosen for optimal sensitivity and linearity. It should be noted that the droplet-generator-based SLM data in Figure 3 exhibits superior sensitivity and linearity compared to previously published data (20). A modified optical system which provides a much narrower radiation path through the analytical flame was employed to obtain these data, and accounts for this improvement.

Figure 3 indicates that for Ca, the linear range of the present SLM system is approximately twice that obtainable with the original SLM system (extending to absorbances of approximately 0.3 and 0.15, respectively), though still less than that obtainable with a line source (curvature appearing at an absorbance of about 0.5). Also, the new SLM system is approximately 1.8 times more sensitive for Ca than the original SLM system, while the hollow cathode data shows a further gain over the new SLM system of approximately 1.2 times.

As mentioned in the foregoing discussion, the linearity and sensitivity exhibited by the SLM technique are directly related to the peak fraction of

incident radiation absorbed by the modulating atoms. Accordingly, to compare the new and previous SLM systems, a Ca hollow cathode lamp was used to determine the approximate peak fraction absorbed by atoms within the modulating droplet clouds (previous SLM system) and within the modulating slot flame (present SLM system). For the modulating solution concentrations used for curves B and C in Figure 3, the approximate peak fractions absorbed were measured to be 57% and 40%, respectively. Because this difference is much smaller than, for example, that between the 5 and 20 $\mu\text{g/ml}$ Ca modulating solutions in Figure 2, it can be inferred that most of the improvement in sensitivity and linearity exhibited by the new SLM apparatus (compared to the droplet-based SLM device) accrues from optical design improvements.

SLM calibration curves obtained with the present system for copper, iron, and lead are shown in Figure 4. While the linear range (in terms of absorbance) of the copper calibration curve appears similar to that seen for Ca (cf. Figure 2), no linear region is discernible in the calibration curves for iron and lead. There is a fundamental reason why greater curvature might be expected in SLM calibration data for these two elements.

Parsons, et al. (29) have estimated the half-widths for the Ca, Cu, Fe, and Pb absorption lines used here, in an air/ C_2H_2 flame, to fall in ranges as follows: Ca ($0.039 \rightarrow 0.025 \text{ \AA}$), Cu ($0.022 \rightarrow 0.015 \text{ \AA}$), Fe ($0.015 \rightarrow 0.012 \text{ \AA}$) and Pb ($0.008 \rightarrow 0.006 \text{ \AA}$). Clearly, the selective modulation process is based on the modulation and detection of radiant power over a very narrow spectral band. However, the measured amplitude of the SLM P_0 or 100% T signal is determined not by the peak change over this narrow band, but by the periodic change in the integrated radiant power over the monochromator bandpass as modulation occurs. Therefore, for a given peak absorption by atoms within the modulating flame, the magnitude of the measured SLM P_0 signal will decrease as the width of the atomic

absorption line decreases. Therefore, an increased peak absorption will be needed to maintain a constant SLM P_0 amplitude (and thus P_0 S/N) with decreasing absorption line width of the modulating atoms.

In accordance with the foregoing considerations, it is not surprising that Ca and Cu working curves exhibit comparable linearity, since their absorption line half-widths are not greatly different. In contrast, the significantly narrower lines of Pb and Fe require far greater peak absorption by the modulating atoms (i.e., greater modulating solution concentration) to produce similar SLM P_0 levels (and thus P_0 S/N ratios). As was mentioned previously, the observed decrease in linearity for these elements can be attributed to this increase in peak absorption by the modulating atoms. This situation is aggravated in the case of Pb because its resonance line lies at a short wavelength, where the primary source radiance is low and the contribution from shot noise is increased. Thus, an even larger SLM P_0 signal is required for Pb in order to maintain a useful signal-to-noise ratio.

SLM Noise Characteristics. The foregoing considerations deal only with SLM signal levels and not with associated noise. For an evaluation of detection limits and precision, however, it is necessary to explore the noise sources in the SLM instrument. In this exploration, it is most meaningful to compare the SLM device with a medium-resolution AAC system. Because the important noise types in AAC and SLM are similar to those in line-source AA, let us first examine these AAL noise sources. The major noise sources contributing to AAL spectrometry have been thoroughly treated by Ingle and co-workers (30-32), and were found to be:

- 1) source flicker noise (arising from fluctuations in source radiance).

2) flame transmission flicker (caused by fluctuations in the transmission characteristics of the analytical flame itself).

3) analyte absorption flicker (due to fluctuations in the absorbance of the sample atoms in the analytical flame).

4) analyte emission flicker noise (generated by fluctuations in the sample atomic emission intensity).

5) signal shot noise (from quantum and secondary emission noise associated with the photomultiplier).

The first three noise sources are all types of proportional or multiplicative noise with respect to the primary source used in the system (Bower and Ingle (30) have recently stated that analyte absorption flicker noise only approximates a proportional noise source). That is, for detection electronics having a given response bandwidth (Δf), the amplitudes of these noise sources will be directly proportional to the source radiant power reaching the photodetector. For example, the flame transmission flicker noise amplitude would be expected to double if the source power reaching the analytical flame (and therefore photodetector) were to double, all other conditions being constant.

These multiplicative noise sources should be contrasted with the fourth and fifth sources listed, both of which are of the additive type. The amplitude of the rms shot noise is related to the total radiant power reaching the photodetector (including radiation from the source, flame background, and sample atomic emission) by the well-known square-root relationship (27), while the analyte emission flicker noise is independent of source intensity.

All the above noise sources are expected to contribute to the total noise in AAC and SLM as well, although greatly different system characteristics must be considered in these latter cases. These differences are discussed qualita-

tively below.

Source Flicker Noise. Flicker noise associated with high-pressure xenon short arc lamps can be taken from manufacturer's specifications to be between 1% and 5% peak-to-peak, depending on power supply, lamp age, and input power rating, and assuming observation over a wide frequency band (Δf). The lamp used in this work was recently found to exhibit approximately 0.6% peak-to-peak noise (with spatial selection for maximum S/N) when measured with DC detection electronics of $\Delta f = 0.5$ Hz. By comparison, Bower and Ingle (30) examined a series of hollow cathode lamps using a measurement system with $\Delta f = 0.5$ Hz and found relative standard deviations whose average was 4.7×10^{-4} (equivalent to 0.24% peak-to-peak noise).

As a result of the greatly different optical spectral bandwidths which are detected, source flicker noise affects AAC and SLM quite differently. In conventional medium-resolution AAC, the effect of this kind of noise is exaggerated because the spectral region viewed by the monochromator is 10-100 times wider than the atomic absorption line being observed. Therefore, most of the observed radiation can not undergo atomic absorption (i.e., lies outside the atomic line), yet still contributes source flicker noise to any AAC measurement.

In contrast, in the SLM technique, radiation is detected over the extremely narrow spectral bandwidth defined by the absorption line of the modulating atoms. Therefore, only the source flicker noise arising from the modulated spectral region results in a multiplicative noise component in the SLM signal. Source flicker resulting from unmodulated radiation within the monochromator bandpass represents an additive noise source, which is removed through the modulation process. While the relative source flicker noise on the SLM signal

can be no smaller than that of the lamp itself (for equal Δf), it is expected to be significantly less than that observed in AAC.

Although less obvious, such source flicker noise considerations also apply to the source drift (i.e., very low frequency source flicker) which is especially troublesome in arc sources. That is, a 1% drift in source power will cause a 1% change in the SLM signal, because only the change in radiant power over the region where the sample atoms absorb will be detected. However, in AAC, a 1% change in radiant power over the entire monochromator bandpass will be detected, even though the sample might absorb less than one tenth of that integrated power. Thus, a much larger relative error should exist in the AAC than in the SLM measurement.

Flame Transmission Flicker. In a way similar to source flicker, flame transmission flicker noise is expected to have a pronounced effect on medium-resolution AAC. Background flame absorption is caused by molecular species present in the flame, and is therefore characterized by broad absorption bands. Because such bands often absorb radiation across the entire spectral region isolated by the monochromator, the flame transmission flicker noise in an AAC measurement will be proportional to the total radiant power reaching the photodetector.

The effect of flame transmission flicker noise in the present SLM system is somewhat more complex than that of source flicker. Transmission flicker in the analytical flame is detected only over the modulated spectral region, much as is source flicker noise. However, the modulating flame appears in the observed light path periodically (at the modulation frequency, f_m) so that any transmission flicker it exhibits is modulated as well and appears at f_m . Thus, modulating flame transmission flicker is multiplicative and is not attenuated

by modulation. Because no spectral narrowing is involved in this background modulation process, modulating flame transmission flicker is detected over the entire background absorption band or monochromator bandpass, whichever is narrower. The relative effect of flame transmission flicker in the present SLM system is therefore expected to be similar to that in AAC, with its importance being intensified for spectral regions of strong flame absorption (i.e., near 200 nm and 300 nm for the air/C₂H₂ flame).

By the same reasoning, any transmitted or reflected radiant power fluctuations caused by imperfections in the chopper mirror employed in the present system will also be detected over the entire monochromator bandpass. Accordingly, minor irregularities in the mirror surface can result in significant noise on the SLM signal.

It should be noted that the constant presence of the modulating flame within the light path in the droplet-based SLM system (20) permits detection of that flame's transmission flicker noise over only the modulated bandpass. Flame transmission flicker noise should therefore be less significant in that earlier SLM design than in the present one.

Analyte Absorption and Emission Flicker. Because analyte absorption flicker represents a multiplicative noise source which is narrow-band (i.e., occurs only over an atomic absorption line), its effect will not be reduced by the selective modulation process but will be quite similar for AAC and SLM. The presence of two absorbing flame cells in SLM does, however, tend to increase the contribution from this noise source, to

Analyte emission flicker is also inherently narrow-band, but is an additive noise source. Due to its additive nature, this noise source can be removed by conventional modulation of the source, as is normally done in AAC. In SLM, the emission from the modulating atoms must appear at the selective

modulation frequency and does add a small emission flicker component to the signal. In addition, the present SLM configuration would allow a small fraction of the sample atom emission to be modulated, although both this emission and the associated flicker noise have proven negligible in these studies. Obviously, conventional modulation of the source in SLM could be employed to alleviate the effects of this noise source.

Shot Noise. The total shot noise observed in both SLM and AAC will be proportional to the square-root of the integrated radiant power arriving at the photodetector, nearly all of which will result from the continuum source. Unlike the noise sources previously discussed, shot noise has an essentially flat noise power spectrum (i.e., has white noise character). Because the shot noise contribution over a given response bandwidth (Δf) is the same at 30 Hz as it is at 0 Hz (d.c.), no modulation process will reduce shot noise and it will therefore contribute equally to both SLM and AAC measurements. The relative significance of shot noise in both techniques will increase at wavelengths near 200 nm due to reduced source output.

Zero %T Noise. A final noise characteristic of the SLM system involves the noise associated with the 0%T signal. In line-source AA employing, for example, a mechanically chopped line source, the 0%T signal is established with the lamp radiation blocked, and with solvent being aspirated into the analytical flame. Therefore, the only noise sources which contribute to the measurement are flame background emission flicker and associated shot noise, photomultiplier dark noise, and electronic noise, all of which are ordinarily small. However, in the SLM technique the 0%T signal is measured with the light source on, both flames lit, and with solvent being aspirated into both flames. Therefore, such important noise

For modulating solution concentrations above 50 $\mu\text{g/ml}$, the increase in P_0 and P signal-to-noise ratios is not enough to offset the loss of absorption sensitivity which results from the large peak absorption depth of the modulating atoms. Therefore, detection limits become worse with increasing modulating solution concentration beyond 50 $\mu\text{g/ml}$.

Table II lists detection limits for several elements obtained in this laboratory for medium-resolution AAC and for the present SLM system. The elements listed are among those usually determined in air/ C_2H_2 flames and whose preferred analytical absorption lines cover a wide wavelength range. No attempt was made to optimize such parameters as fuel/oxidant ratio, flame viewing region, and monochromator slit width for each element. Through such optimization, some improvement in detection limits would be expected, although the medium-resolution AAC values found here are similar to those cited by others (16).

The data in Table II show that the detection limits found using the present SLM system are approximately equal to those obtained in this laboratory using AAC, with SLM detection limits for lead (216.9 nm) and zinc being poorer than those for AAC. These SLM detection limits are somewhat disappointing, particularly considering the expected reduction of source flicker noise in SLM compared to AAC. In order to understand why the SLM and AAC detection limits are similar, more information is needed concerning the limiting noise sources in these two methods.

Accordingly, a preliminary investigation was performed employing a sequential elimination of system noise sources similar to that described by Bower and Ingle (30,31) to determine which noise sources limit detection in the AAC and SLM arrangements. Tests were carried out at the calcium 422.7 nm line, due to the lack of flame absorption and ample source intensity at that wavelength.

The results of this preliminary study indicate that the limiting noise

sources as source-induced shot noise, chopper-induced flicker noise, and modulating flame transmission flicker noise will still contribute to the 0%T signal measurement, thereby reducing the attainable precision.

To the authors' knowledge, noise involved with selective-modulation AAC has been considered previously only once (18). In that treatment, which involved a sample modulation approach to selective modulation, it was indicated that the selective modulation process could remove the effect of source flicker noise from the measured absorption signal. A recent publication has also cited sample modulation as a possible means of reducing "lamp transmission noise" (apparently referring to lamp flicker noise) in AAL (30). In light of the preceding discussion, it seems very unlikely that relative source flicker noise could be significantly reduced below that typical of the source itself by such a modulation process.

Detection Limits. As previously mentioned, the best SLM modulating solution concentration for working curve sensitivity (slope) and linear range might not be optimal in terms of S/N and detection limit. Figure 5 shows the change in calcium detection limit over a range of calcium modulating solution concentrations. From Figure 5, the best calcium detection limit is obtained using a modulating solution concentration of about 50 $\mu\text{g/ml}$ for this particular experimental arrangement, in contrast to the 5 $\mu\text{g/ml}$ value required for greatest linearity and sensitivity.

The observed improvement in SLM detection limit with modulating solution concentrations below 50 $\mu\text{g/ml}$ indicates that modulation depth can be increased over a substantial range while noise remains essentially constant. This behavior suggests that the limiting noise sources in the present SLM system are proportional to total integrated light intensity, which changes little with modulation depth.

source in an AAC measurement at this absorption line is source flicker noise. While the previous noise discussion suggests that both source-induced shot noise and analytical flame transmission flicker could be significant in AAC, both proved to be much smaller than source flicker in this case.

Furthermore, the limiting noise source in an SLM calcium measurement appears to be chopper-induced flicker noise. For the present SLM system, modulating flame transmission flicker is less than half as large as chopper-induced flicker at the calcium line. As expected, the source flicker noise contribution in SLM is minor compared to that of the above mentioned noise sources. Shot noise too is insignificant here, as would be indicated by its minor importance in our AAC measurements.

This preliminary determination of limiting noise sources suggests that the similarity of the SLM detection limits to those found for AAC does not indicate a fundamental SLM limitation. It appears that while the limiting AAC noise source (source flicker noise) is substantially reduced in the SLM technique, most of this potential S/N advantage is lost in the present SLM design through flicker noise introduced by the mirrored chopper. Like calcium, most of the elements listed in Table II occur in spectral regions of ample source output power and relatively low air/C₂H₂ flame absorption. Therefore, with the exception of lead (216.9 nm), zinc, and cadmium, noise sources which are limiting for calcium are also expected to be limiting for the other elements listed in Table II, and similar AAC and SLM detection limits are not surprising. However, because of the greatly reduced source output power and increased flame absorption exhibited at the three shortest absorption wavelengths, the importance of both shot noise and flame transmission flicker will be increased for both SLM and AAC determination of the corresponding elements. Light loss due to background modulation in the present SLM system further complicates the shot

noise problem. At the lead 216.9 nm line, for example, the mismatch of beam-splitter transmittance and reflectance produces a background modulation of about 30%, compared to only 5.5% at the 324.7 nm copper line. In addition, absorption by the modulating flame increases background modulation at 217 nm to about 50%. The low source output at this short wavelength and the loss of half of the available radiant power-to-background modulation combine to further increase the significance of shot noise; these factors account for an SLM detection limit for lead which is poorer than that obtained using AAC. A similar background modulation effect is seen for zinc, and to a lesser extent for cadmium.

Much of the background modulation problem should be avoidable through use of a more suitable beam splitter or by substitution of two phase-linked choppers for the present beam splitter and chopper. In addition, use of a shorter path-length modulating flame could help to reduce background modulation, with the decreased path length being offset by higher modulating solution concentrations to maintain useful modulation depths. Both methods of reducing background modulation would lead to much more efficient use of available light in the system, particularly at short wavelengths.

Significantly, the previous droplet-generator-based SLM system (20) did not suffer from the chopper-induced flicker noise which has proven to be limiting in the present system, nor did that SLM device entail background modulation and the associated light loss just described.

Background Modulation Caused by Molecular Absorption. Although modulating flame absorption and optical imperfection lead to some background modulation, such modulation can be easily overcome as explained in the experimental section. That is, during solvent aspiration into the modulating flame and before any

modulating solution is aspirated, the full magnitude of the background modulation can be detected and either suppressed or recorded and subtracted from later SLM data obtained at the same wavelength.

However, several elements form molecular species which exhibit absorption bands within flames (33-35). It is therefore possible that a modulating solution would contain an element having an analytical absorption line on top of the molecular absorption band of another element present in the same solution. Any attempt to use the analytical line for selective modulation would then result in a concomitant broad-band modulation component of unknown magnitude due to the molecular band. Not only will a simple nulling procedure then not suffice for measurements made at the analytical line, but the problem could easily go unrecognized and lead to erroneous sample absorbances.

Of course, the overlap of a useful absorption line with a strong molecular absorption band is not common, and such absorption bands will not be troublesome when moderate elemental concentrations are involved. The elemental combinations that do exhibit such overlap should, however, be avoided in modulating solutions or appropriate corrections applied. Combinations which present such possibilities of interference include the overlap of the Li 670.8 nm line with SrO bands; overlap of the Ba 553.6 nm line with a CaOH band; overlap of the Na doublet at 589 nm and 589.6 nm with a CaO band; and overlap of the Cr 357.9 nm line with the edge of MgOH bands (33). Because many of these bands are quite weak, it is unlikely that they would cause significant error in calculated absorbances and their effect could be disregarded at the modulating concentrations typically used for SLM. If even this small error cannot be tolerated, however, the procedure outlined below can be employed.

The interference chosen to experimentally demonstrate this correction

method is one of the strongest interferences listed above, that of the CaOH band (550 - 560 nm) on the analytically important 553.6 nm Ba absorption line. The correction procedure which was tested involves an off-line measurement of the modulated signal to determine what fraction of the total signal at the atomic line is contributed by the broad band. Once determined, that contribution can be subtracted from SLM P_0 and P values.

To demonstrate this correction procedure, one modulating solution containing only Ba at 1000 $\mu\text{g/ml}$ and a second containing 1000 $\mu\text{g/ml}$ Ba and 100 $\mu\text{g/ml}$ Ca were prepared. A 500 $\mu\text{g/ml}$ Ba sample solution containing no Ca was also prepared. It should be noted that the Ba concentrations used are unusually high due to the poor atomization of Ba in the air/ C_2H_2 flame. Potassium concentrations of 2000 $\mu\text{g/ml}$ and 1000 $\mu\text{g/ml}$ were also included in the modulating and sample solutions, respectively, to suppress Ba ionization. Due to the Ba line and CaOH band emission from the modulating flame, an emission correction was applied to all data before absorbances were calculated.

Figure 6 shows the SLM P_0 signal recorded over 550-560 nm spectral range for the Ba + Ca modulating solution (i.e., this scan represents the output of the combination source over this wavelength region). The band structure due to the CaOH absorption band is clearly shown in the figure, and contributes about 20% of the total detected SLM P_0 signal at the Ba line. Although one might argue that a greater relative interference should be used for such a correction test, it should be noted that the Ba concentration in the modulating solution was chosen to provide nearly the minimum useful modulation depth (approximately equal to that obtained for a 10-15 $\mu\text{g/ml}$ Ca modulating solution at the Ca 422.7 nm line), and that the Ca modulating solution concentration employed here is about five times that normally used for SLM, in order to provide a more severe test situation than would ordinarily be encountered.

To perform the test, the modulating solution containing only Ba was first aspirated to carry out a normal SLM absorption measurement of the Ba concentration in the sample solution. This measurement was then repeated, except that the modulating solution containing both Ba and Ca was employed. If broad-band modulation were indeed significant, this latter measurement should produce an erroneously low sample absorbance. Finally, the sample absorbance was again determined using the Ca + Ba modulating solution, except this time an off-line correction technique was employed, in a way similar to that used to overcome broad-band flame background emission in flame emission spectrometry. In this procedure, the 0% transmittance level is set while the desired modulating solution is aspirated (instead of merely solvent) and with the monochromator moved adjacent to the Ba line (to 553.2 nm). After nulling the background at this off-line wavelength, the monochromator was scanned back to the Ba line and the sample absorbance determined as usual.

Table III lists the three absorbance values obtained in the correction test and their 95% confidence limits. It is seen that the uncorrected absorbance obtained using the Ba + Ca modulating solution is about 15% low, while that obtained using off-line correction matches the true absorbance value within confidence limits.

Like the flame-background-correction technique used for flame emission spectrometry, this off-line correction method can be more complicated when the interfering absorption band changes rapidly with wavelength in the spectral region where it overlaps the analytical line of interest. In fact, the difference in the magnitudes of the absorption band on the two sides of the Ba line used here (see Figure 6) suggests that an improved correction might have resulted from using the average of the magnitudes on opposite sides of the line rather than the magnitude on only one side. However, due probably to the

small relative magnitude of the absorption band in this case, the present, simplified off-line correction was sufficient. Essentially all of the methods which have been developed to cope with similar problems in emission spectrometry could be easily adapted to this off-line SLM correction technique. These methods are well documented (24,36) and need not be discussed here.

Stray Light Considerations. Because of the high radiant powers and wide spectral range emitted by the continuum sources ordinarily used in AAC, stray light within the monochromator is expected to be troublesome, particularly near the wavelength limits of the optical components and detector. Zander et al. (16), for example, have reported that AAC performed with an echelle monochromator results in 5% of the radiation reaching the detector at 230 nm being stray radiation. Moreover, stray radiation at the 213.8 nm Zn line causes a significant reduction in both absorption sensitivity and working curve linearity, if one does not correct for it.

In a similar test to that reported (16), but involving the medium-resolution monochromator used in the present work, stray light was checked from 200 nm to 285 nm and found to vary little with wavelength, probably indicating simple scattering of continuum radiation within the monochromator. As expected, the worst stray-radiation-to-signal ratio occurred at short wavelengths, with 1.5% of the radiant power reaching the photomultiplier tube at the 213.8 nm zinc line resulting from stray radiation. The relative magnitude of the stray radiation decays to approximately 0.3% at the 248.3 nm iron line, due to the increased source output and greater photomultiplier tube response at this longer wavelength.

One significant advantage of the SLM technique is its virtual immunity to such stray light interference. Because only radiation over an extremely

narrow spectral region is modulated (i.e., the width of an atomic absorption line), no selective modulation of stray light occurs. For this reason, any stray radiation goes undetected by the frequency-selective electronics. In this sense, the selective modulation apparatus acts essentially like an extremely narrow pre-filter for the monochromator, but with the versatility to have both the number of filter pass bands and their central wavelengths easily modified.

Because of the broad-band modulation which can occur in the present SLM system, it is possible for some portion of the stray radiation to occur at the modulation frequency. However, any such modulated stray radiation is also present when the system 0%T is being set and is automatically nulled out at that time along with any other background modulation. While stray radiation contributes a finite amount of noise to any SLM measurement, its effect should be very small, in view of the low level of stray radiation exhibited even at short wavelengths.

CONCLUSION

Through use of burner types, solution introduction methods, and modulation techniques similar to those employed in common AAL instruments, the new SLM system described herein provides the reliability and ease of operation necessary for routine analytical work. In addition, such SLM characteristics as high absorption sensitivity, useful linear range, simplified background correction, and extremely narrow effective spectral bandwidth are retained.

However, the new modulation method exhibits several limitations as well. Due to the double-beam arrangement employed, the flicker noise associated with the modulating flame and chopper mirror is detected over the entire monochrom-

ator bandpass, and the latter noise source appears to be the precision-limiting component for SLM measurements using the system. In addition, background modulation resulting from the beam-splitting operation and from absorption within the modulating flame causes light losses which can become severe at short wavelengths, thereby aggravating shot noise problems at these wavelengths. Because background modulation is a function of wavelength, spectral scanning is also hindered by the need for separate baseline correction. It is expected that use of a more suitable beam-splitting scheme and a shorter path modulating flame will reduce background modulation. A shorter path modulating flame will also reduce the magnitude of flame transmission flicker noise.

While the authors consider the detection limits and precision obtainable with the new SLM system to be entirely satisfactory for many analytical applications, they could be improved, since the noise sources limiting detectability are not fundamental to the SLM technique. With increased understanding of the dominant noise sources within the present system, it is expected that modifications in the device used to perform the selective modulation will permit substantial improvements in detection limits for future SLM system designs.

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CREDIT

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TABLE I EXPERIMENTAL COMPONENTS AND CONDITIONS

| | |
|--------------------------------------|---|
| Continuum Source | 300-W Eimac illuminator with aluminum-coated parabolic collimator (No. VIX-300UV), used with fan-cooled housing No. R-300-1), and powered by a current-regulated power supply (No. PS300-1, Varian Eimac Division, San Carlos, Calif.). |
| Hollow Cathode Lamp | Calcium lamp, operated at 15 mA (Type WL-22610A, Westinghouse, Elmira, N.Y.). Powered by a regulated power supply (No. EUW-15, Heath Co., Benton Harbor, Mich.) and series potentiometer. |
| Burners and Flames | 10 cm slot burners used for both analytical flame (No. AB51, Varian Techtron, Walnut Creek, Calif.) and modulating flame (No. 24036-02, Instrumentation Laboratory Inc., Lexington, Mass.). Air/C ₂ H ₂ flames used exclusively. |
| Observation Height | Both analytical and modulating flames observed approximately 1 cm above burner tops. |
| Gas Handling | Described previously (20) |
| Gas Flow Rates (corrected to STP) | 17.3 L/min. air and 3.12 L/min. acetylene. Identical flows used for analytical and modulating flames. |
| Solution Introduction | Spray chambers and pneumatic nebulizers used for solution introduction into analytical flame (Perkin-Elmer Corp., Main Ave., Norwalk, CT.) and modulating flame ("Counter-Flo Jet" type, Instrumentation Laboratory, Lexington, Mass.). Analyte and modulating aspiration rates, 3.0 and 4.3 ml/min., respectively. |
| Monochromator | Described previously (20). Spectral slit width = 0.1 nm for all work reported. |
| Optics | L ₁ , diameter = 2.5 cm, F.L. = 10 cm. L ₂ , diameter = 2.5 cm, F.L. = 2.5 cm. L ₃ , diameter = 2.5 cm, F.L. = 7.5 cm. L ₄ , diameter = 2.5 cm, F.L. = 15 cm. Lens material is Suprasil I. M ₁ , diameter = 2.5 cm. M ₂ , diameter = 5.1 cm. Mirror surfaces are UV-enhanced aluminum (Mirrors and lenses from Melles Griot, 388 Main Street, Danbury, CT.). Beam splitter, diameter = 2.5 cm, approximately 30%T, 30%R over 200-400 nm range (no. 6-1325 U, Special Optics, Little Falls, N.J.). |
| Chopper | Half-mirrored chopper, mirror diameter = 11.5 cm; aluminum surfaced. Rotated at 30 Hz (1800 r.p.m.) via synchronous motor. |

TABLE I (continued)

| | |
|-------------------|---|
| Photomultiplier | RCA 1P28 photomultiplier tube, operated at approximately 450V. Powered by a regulated high voltage supply (No. 245, Keithley Instruments, Inc., Cleveland, Ohio). |
| Signal Processing | As previously described (20). |

TABLE II COMPARISON OF DETECTION LIMITS^a
BETWEEN CONTINUUM-SOURCE (AAC)
AND SELECTIVE SPECTRAL-LINE MOD-
ULATION (SLM) ATOMIC ABSORPTION
SPECTROMETRIC METHODS

| Element | Atomic Line (nm) | SLM ^b Detection Limits (μg/ml) | AAC ^c Detection Limits (μg/ml) |
|-----------|---------------------|--|--|
| Calcium | 422.7 | 0.025 | 0.065 |
| Copper | 324.7 | 0.066 | 0.13 |
| Lead | 283.3 | 0.49 | 1.05 |
| Magnesium | 285.2 | 0.011 | 0.014 |
| Manganese | 279.5 | 0.12 | 0.16 |
| Iron | 248.3 | 0.32 | 0.42 |
| Cobalt | 240.7 | 0.46 | 0.50 |
| Nickel | 232.0 | 0.80 | 0.82 |
| Cadmium | 228.8 | 0.30 | 0.28 |
| Lead | 216.9 | 1.80 | 1.37 |
| Zinc | 213.9 | 0.21 | 0.15 |

- a. Detection limit defined by St. John et al. (25) to be that concentration yielding a $(P_0 - P)$ value 1.85 times the root-mean-square noise.
- b. Modulating solution concentration chosen to give about 9% modulation depth for Pb (216.9) and Zn and 6% modulation depth for all other elements tested. 50 μm slits used exclusively.
- c. 50 μm slits used exclusively.

TABLE III OFF-LINE CORRECTION OF CaOH BAND INTER-
FERENCE ON Ba 553.6 nm LINE.

| <u>Modulating Solution Employed</u> | <u>Correction Employed</u> | <u>Average Ba Sample^a Absorbance</u> | |
|---|----------------------------|---|-------------------|
| Ba Solution | ----- | 0.45 | .008 ^b |
| Ba + Ca solution | off-line correction | 0.45 | .007 |
| Ba + Ca solution | no special correction | 0.38 | .008 |

a. Represent averages of three trials; 95% confidence limits given.

b. Absorbance without interference.

Figure 1 SCHEMATIC DIAGRAM OF THE DOUBLE-BEAM SLM DEVICE - TOP VIEW.

A_1 is an aperture stop; A_2 is a nulling aperture; F is a field stop; L_1 - L_4 are lenses; M_1 and M_2 are plane mirrors; B.S. is a beam splitter; C is a half-mirrored chopper; R.D. is a reference detector for lock-in amplifier reference signal.

Figure 2 EFFECT OF MODULATING SOLUTION CALCIUM CONCENTRATION ON SLM CALCIUM (422.7 nm) ANALYTICAL CURVES.

- (A) 5 $\mu\text{g/ml}$ calcium modulating solution
- (B) 10 $\mu\text{g/ml}$ calcium modulating solution
- (C) 20 $\mu\text{g/ml}$ calcium modulating solution

Figure 3 CALCIUM (422.7 nm) ANALYTICAL CURVES OBTAINED USING LINE-SOURCE (AAL), PRESENT SLM [SLM (NEW)], AND DROPLET-BASED SLM [SLM (OLD)] ATOMIC ABSORPTION SPECTROMETRY.

5 $\mu\text{g/ml}$ calcium used in SLM (new) modulating solution; 200 $\mu\text{g/ml}$ calcium used in SLM (old) modulating solution.

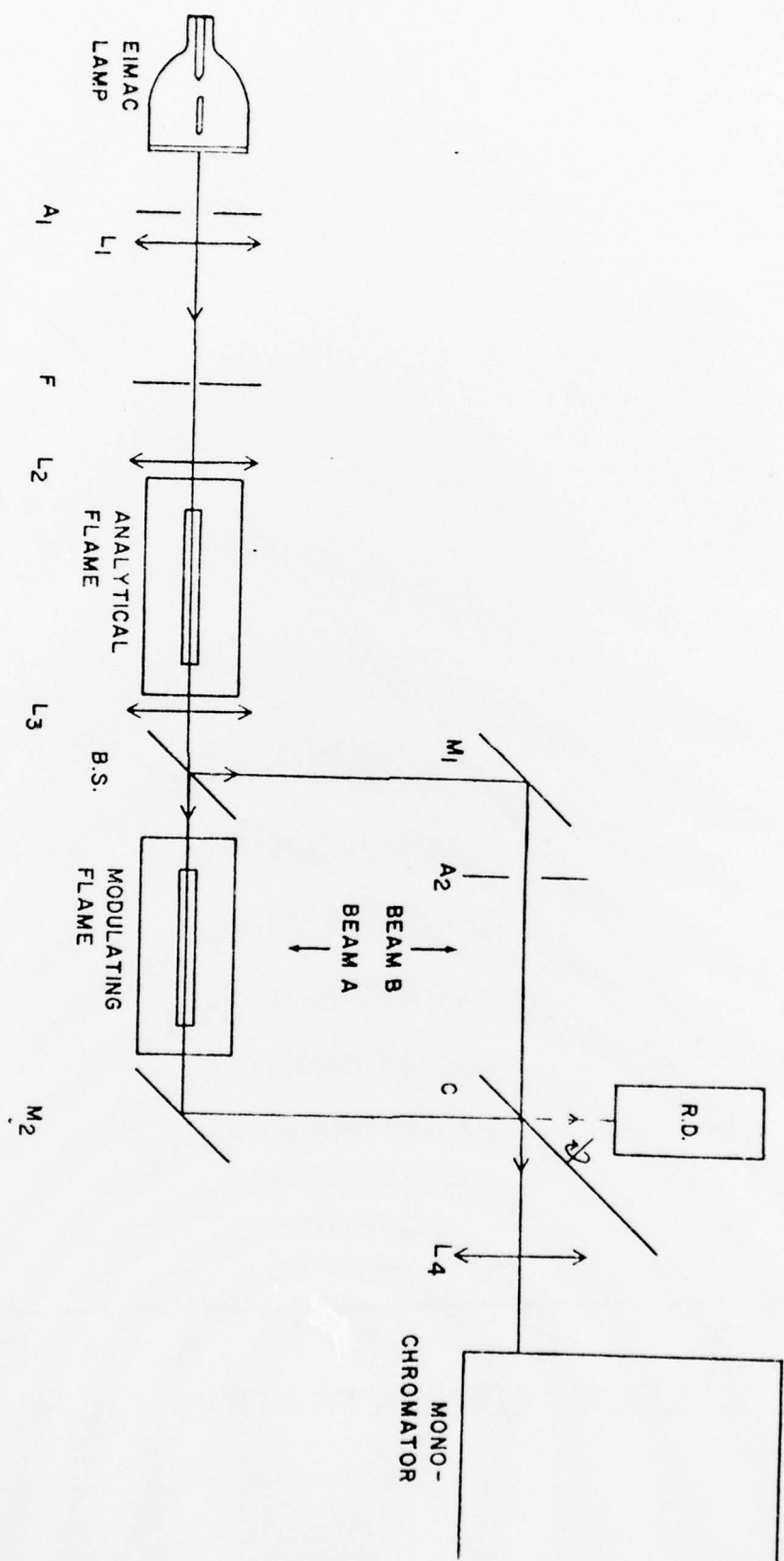
Figure 4 SLM ANALYTICAL CURVES FOR COPPER, LEAD, AND IRON.

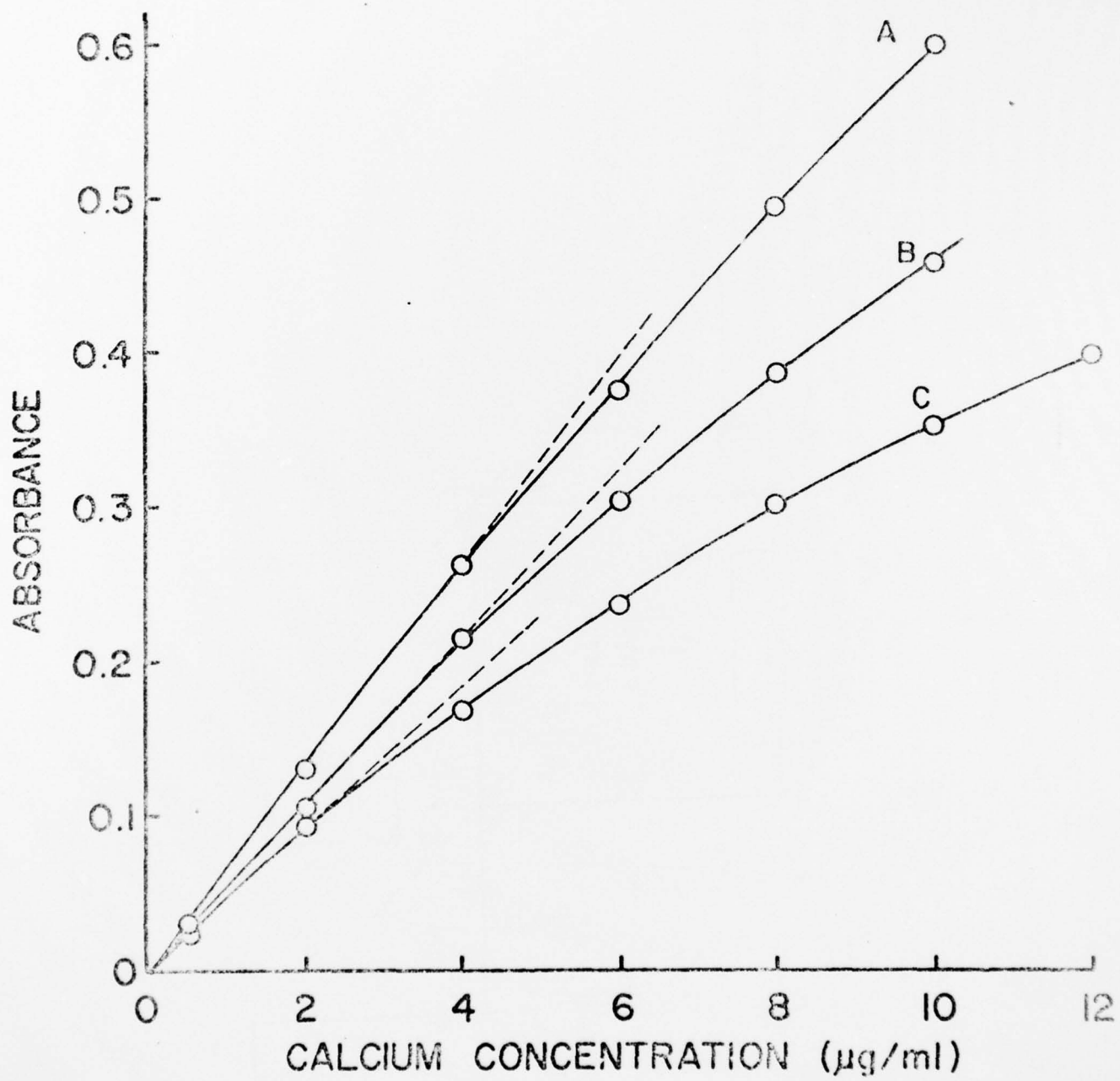
20 $\mu\text{g/ml}$ copper, 500 $\mu\text{g/ml}$ lead, and 100 $\mu\text{g/ml}$ iron used in modulating solutions.

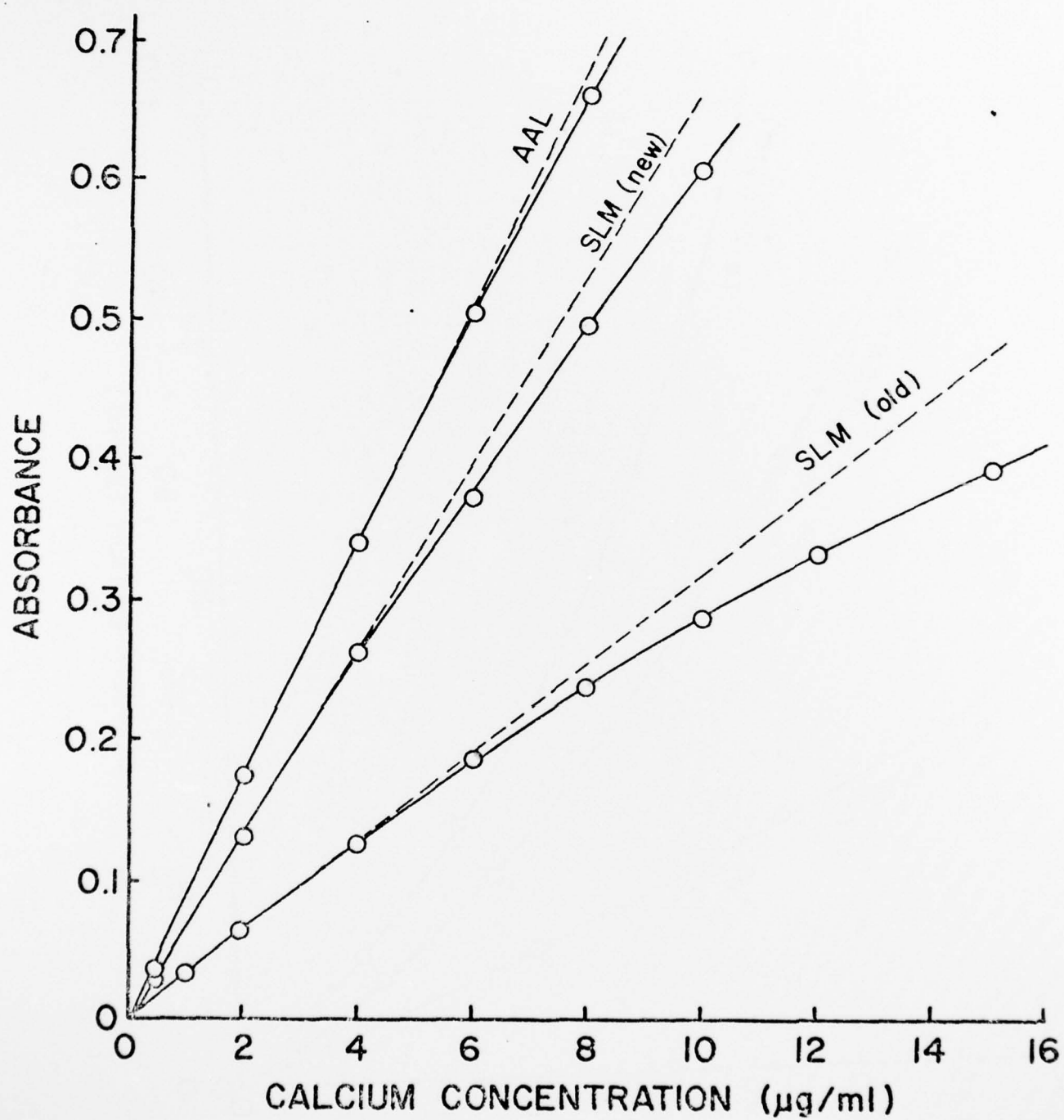
Figure 5 EFFECT OF MODULATING SOLUTION CONCENTRATION ON SLM CALCIUM (422.7 nm) DETECTION LIMIT. SEE TEXT FOR DISCUSSION.

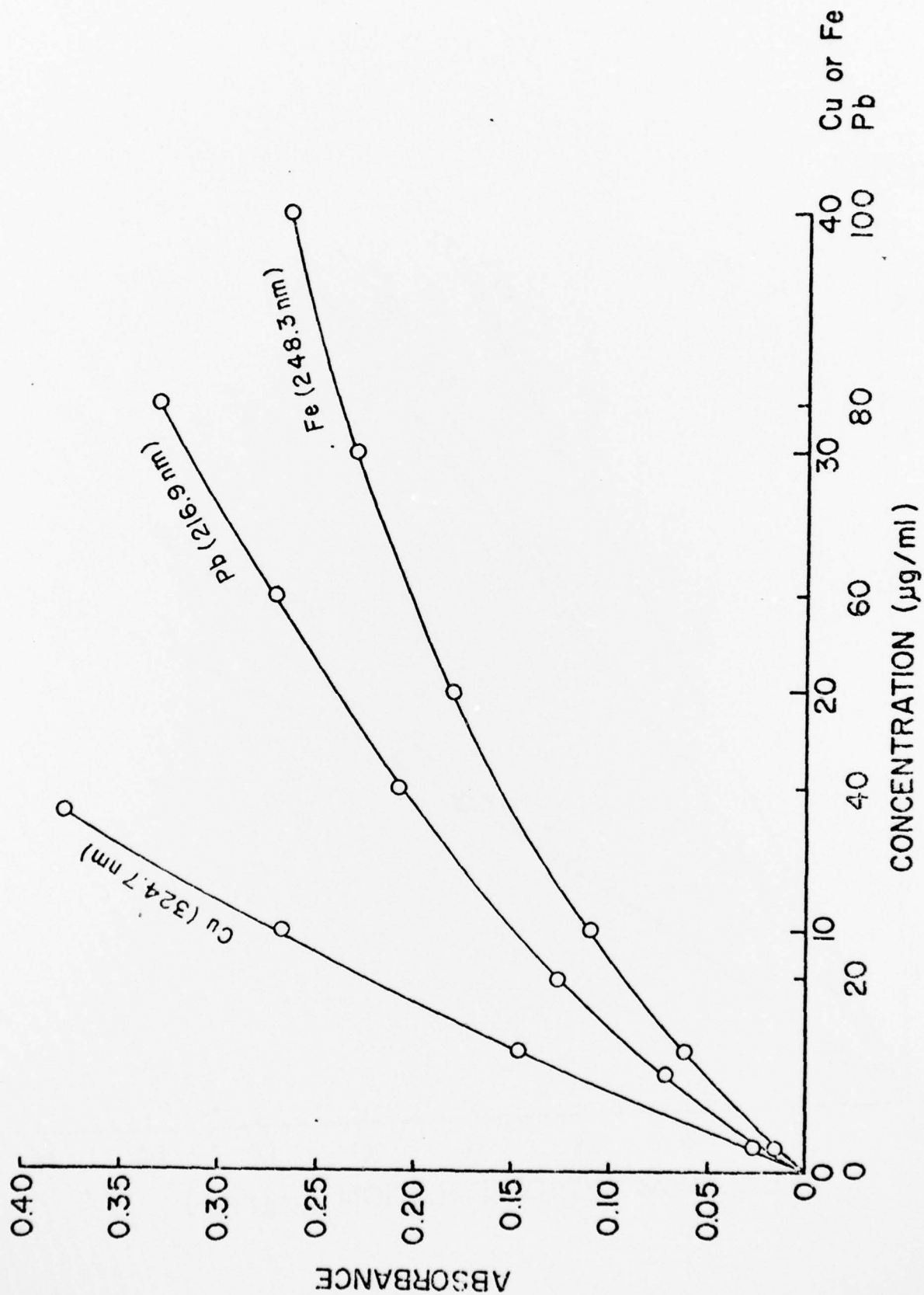
Figure 6 SPECTRUM OF SLM COMBINATION SOURCE SHOWING Ba 553.6 nm LINE AND INTERFERING CaOH BAND.

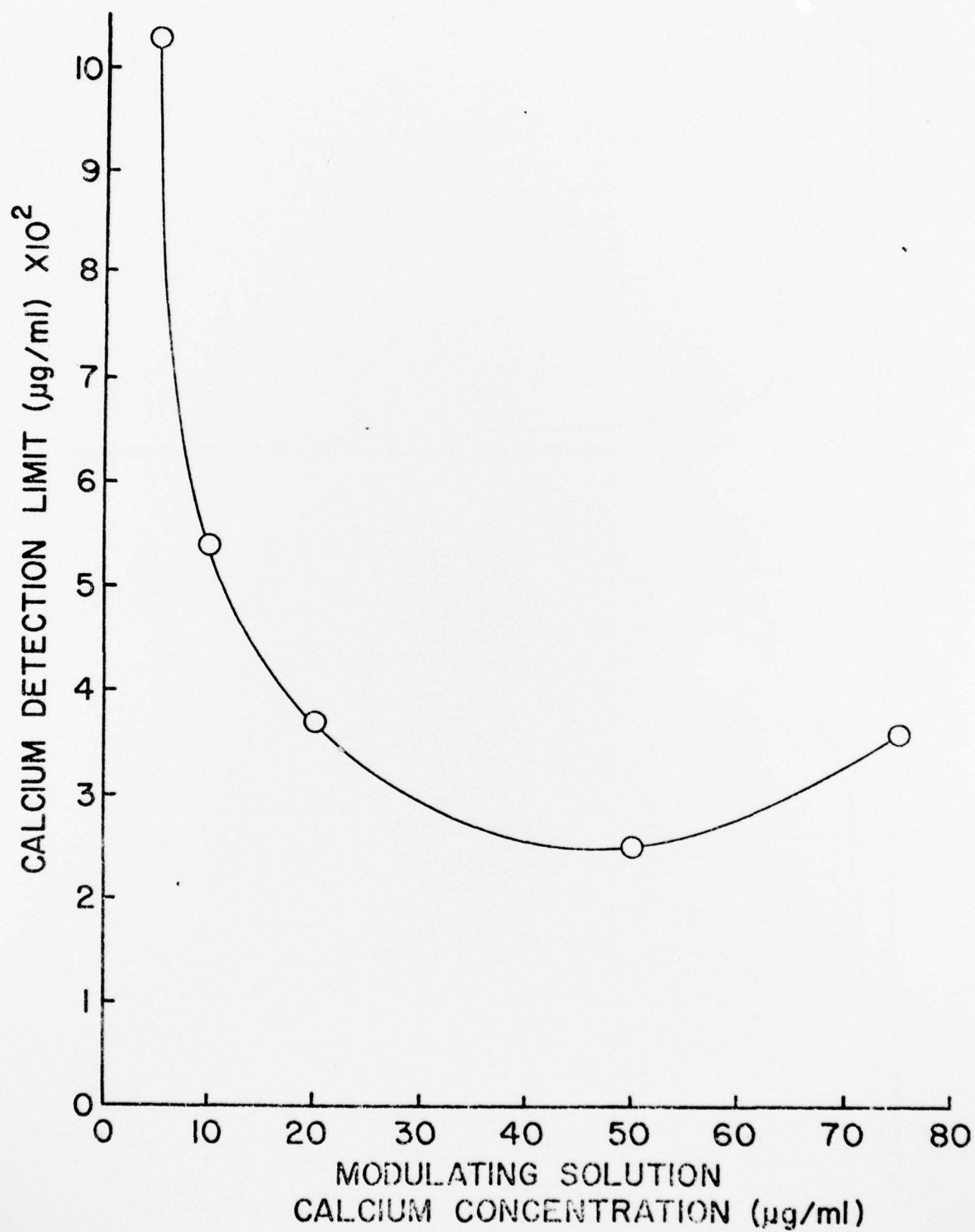
Spectrum corrected for Ba and CaOH emission and background modulation. See text for explanation.

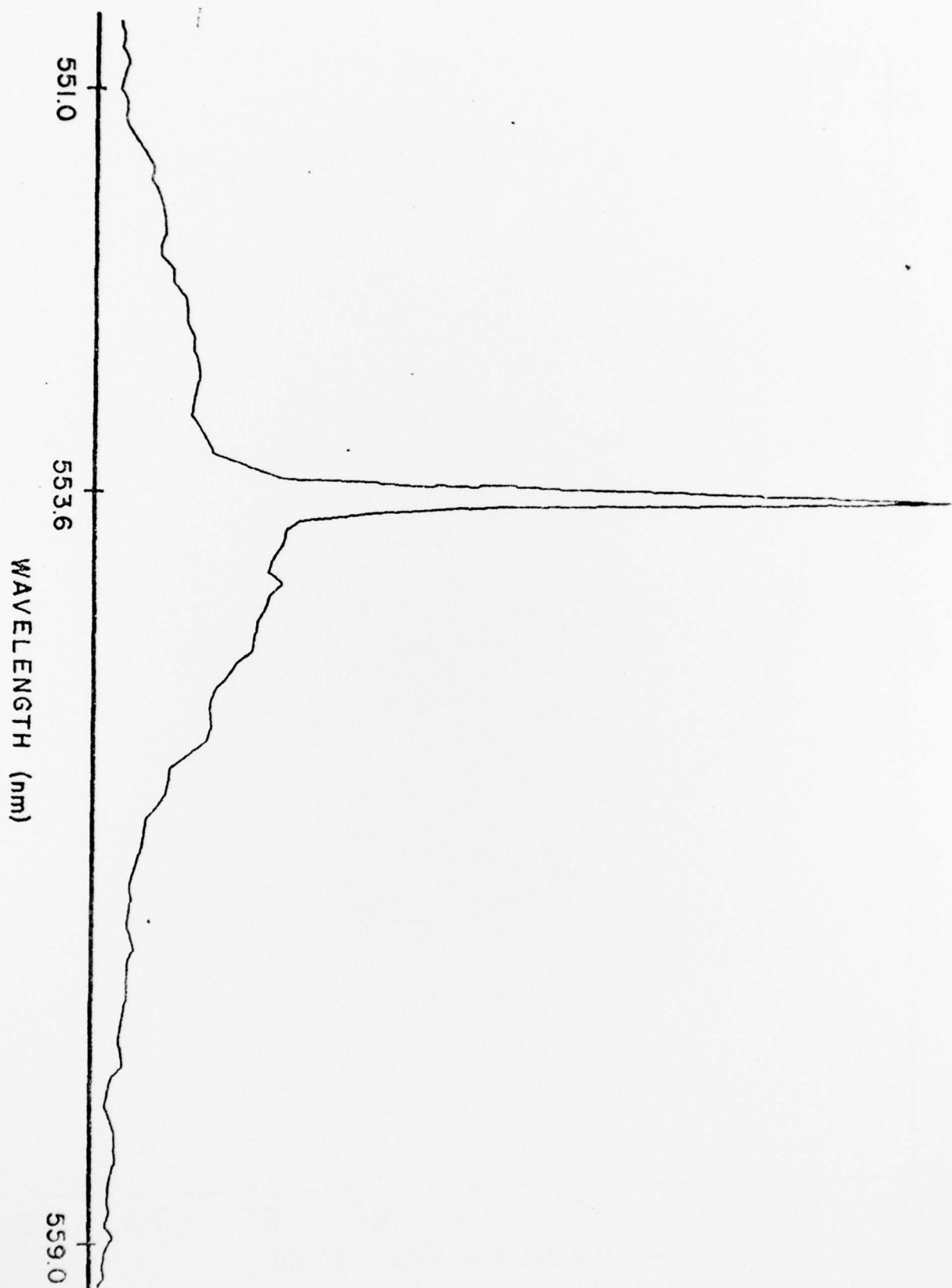












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